

Effect of Addition of Organic Microspheres on Proton Conductivity Property of Sulfonated Poly(arylene ether sulfone) Membrane

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ABSTRACT: Sulfonated poly(arylene ether sulfone) (SPAES)/polystyrene(PS) and SPAES/polystyrene sulfonic acid (PSSA) composite membranes were studied for a proton-exchange membrane used in a fuel cell. PS microspheres were synthesized by emulsion polymerization. PSSA microspheres with 5.3 mmol/g ion-exchange capacity (IEC) were prepared by sulfonation of PS microspheres. The composite membranes were prepared by solution casting. SPAES/PSSA composite membranes showed higher proton conductivity than a SPAES membrane because of the IEC improved by adding PSSA. Although the addition of PSSA also brought about the

increase of a methanol permeability, the proton/methanol selectivity defined as the ratio of the proton conductivity to the methanol permeability was improved at low humidity by adding 5 wt % of PSSA microspheres. Differential scanning calorimetry results indicated that the amount of free water varied in the cases of the addition of the two kinds of organic microspheres. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3739–3745, 2008

Key words: proton-exchange membrane; sulfonated poly(arylene ether sulfone); sulfonated polystyrene microspheres

INTRODUCTION

Direct methanol fuel cells (DMFCs) are promising candidates for portable power sources due to its high energy density and low environmental pollution.¹ A proton-exchange membrane (PEM), which is sandwiched between an anode and a cathode of the cell, plays an important role not only as a proton conductor but also as a methanol barrier.² Hydrated perfluorosulfonic acid membranes, such as Nafion, are typically used as the electrolyte in fuel cells because of their excellent chemical, mechanical, and thermal stability in addition to their high conductivity. Although the Nafion membrane is suitable for fully humidified hydrogen fuel cells, it has an unacceptably high rate of methanol crossover for DMFC application.^{3–5} In this regard, sulfonated aromatic polymer has been recently studied, and some of them showed satisfactory chemical and electrochemical stability for DMFC applications. Of these polymers, poly(arylene ether sulfone) containing sulfonate groups (SPAES) have been extensively investigated as a membrane material of DMFC at high temperature.⁶ However, the proton conductivity of

the membranes in many cases is still low, especially at low humidity conditions.

To improve the proton conductivity and to decrease the methanol permeability of the SPAES membranes, one of the effective strategies is to modify the membrane by some additives. A membrane containing organic or inorganic particles is called a composite membrane. So far, there are many reports to modify a Nafion membrane with particle additives. Park and Yamazaki³ reported the incorporation of calcium phosphate into a Nafion membrane. The composite membranes showed higher proton conductivity than the cast Nafion membrane. Ramani et al.⁷ investigated Nafion-based composite membranes with different inorganic heteropolyacid additives such as phosphotungstic acid and silicotungstic acid. Jalani et al.⁸ synthesized Nafion-MO₂ (M = Zr, Si, Ti) nanocomposite membranes, which exhibited higher water sorption than a Nafion membrane. Other additives such as polyvinyl alcohol,⁹ Pd,¹⁰ silica, and phosphotunglic acid¹¹ were also used in composite membranes. However, little work has been done for using organic particles to modify the membrane. Some of the organic particles can be easily prepared in small sizes by emulsion polymerization and also can be sulfonated to obtain high ion-exchange capacity (IEC) without difficulty. These meet the need of modification of a PEM.

In this article, two different organic particles, polystyrene (PS) microspheres and polystyrene sulfonic

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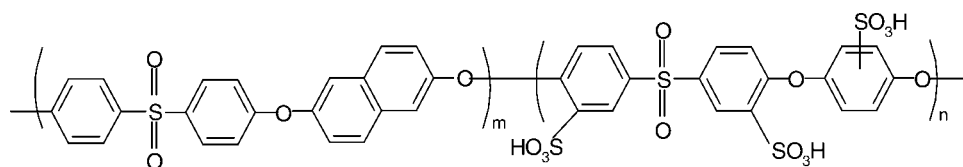


Figure 1 Chemical structure of the SPAES polymer.

acid (PSSA) microspheres, were introduced into the SPAES membranes to investigate the effect of the organic microspheres on the proton and methanol permeability of the SPAES composite membrane. PS microspheres, which were hydrophobic, were expected to decrease the methanol permeability of the membrane. On the other hand, PSSA microspheres, which have high IEC, were thought to improve the proton conductivity of the membrane.

EXPERIMENTAL

Materials

Styrene and divinyl benzene, which served as the monomer and crosslinking agent, respectively, were purchased from Wako Pure Chemical Industries and distilled under reduced pressure before use. Sodium dodecyl sulfate, ammonium peroxydisulfate, concentrated sulfuric acid (95–98%), and *N*-methyl-2-pyrrolidone were also purchased from Wako Pure Chemical Industries and used as received. Sulfonated poly(arylene ether sulfone)s (SPAES) polymer used were synthesized by the nucleophilic substitution reaction according to Ref. 12. The chemical structure of the SPAES polymer was shown in Figure 1. This SPAES was a block copolymer with both hydrophilic and hydrophobic parts. The M_n and M_w of the SPAES polymer were 6.6×10^4 and 1.9×10^5 , respectively. The IEC was 1.8 mmol/g. The mole ratio of the hydrophilic block (n) to hydrophobic block (m) calculated by the IEC value was 25 : 75.

Synthesis of PS and PSSA microspheres

PS microspheres were synthesized by emulsion polymerization.¹³ The styrene and divinyl benzene mixtures (the weight ratio was 95 : 5) were dispersed in an aqueous solution (25 wt %) containing 7 wt % sodium dodecyl sulfate as a surfactant and 0.45 wt % ammonium peroxydisulfate as an initiator. The reaction was carried out in a 250-mL three-necked flask for 6 h in 80°C with the bubbling of nitrogen gas. Then the resulting emulsion was precipitated in a large excess of methanol and separated out by centrifugation.

PSSA microspheres were prepared by sulfonation of the PS microspheres (5 g) by concentrated sulfuric acid (50 mL) for 24 h at 120°C under nitrogen atmos-

phere.¹⁴ Then the microspheres were washed with deionized water to remove the residual sulfuric acid.

Membrane preparation

PS (or PSSA) microspheres were first dispersed in *N*-methyl-2-pyrrolidone (NMP) by ultrasonic processing for 30 min, and then SPAES polymer was added in the solution followed by stirring for 24 h. The resultant suspension was cast on a glass plate by a casting knife. The cast suspension was dried at 80°C for 12 h and then at 100°C for another 48 h to prepare a composite membrane composed of SPAES and organic microspheres. After drying, the membranes were kept in deionized water. The thickness of the wet membranes was about 1 mm.

Characterization of the composite membrane

Particle sizes of the PS and PSSA and their IEC

The microspheres were first dispersed in deionized water at the concentration of about 50 ppm by ultrasonic processing. Then the size distribution of the microspheres was measured by the dynamic light scattering (DLS7000, Otsuka Electronic, Japan). FTIR measurements (FTIR-8000PC, Shimadzu, Japan) were carried out to confirm sulfonic groups on PSSA microspheres. Microspheres were ground into the dry IR-grade KBr to make the KBr-sample pellet containing 1 wt % microspheres. The spectra represent an average of 30 scans taken in the wavenumber range of 4000 cm^{-1} – 400 cm^{-1} .

IEC (mmol/g) was determined by a titration method as follows. Microspheres (0.1 g) were equilibrated in a large excess of 1 mol/L NaCl solution at room temperature for 24 h. The suspension was then titrated with 0.01 mol/L NaOH solution by using phenolphthalein as an indicator.^{13,14}

Membrane IEC and water uptake

IEC of the membrane was determined by the similar method as mentioned earlier. The water uptake was measured by a weight difference methodology. A wet membrane, which was soaked in deionized water at least for 24 h, was weighed and then dried in a vacuum oven at 100°C for 24 h and

weighted again. The equation for water uptake was as follows:

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

Proton conductivity of the membrane

Proton conductivity of the membranes was measured by the AC-impedance method. The temperature was fixed at 50°C with a variety of relative humidity (RH) that ranged from 30 to 90%. The conductivity σ (S/cm) of the samples in the longitudinal direction was calculated by the following equation,

$$\sigma = \frac{l}{RS} \quad (2)$$

where l is the distance between the electrodes used to measure the potential ($l = 1$ cm), R (Ω) is the impedance of the membrane, and S (cm^2) is the cross-sectional area of the membrane.

Methanol permeability through the membrane

The methanol permeability was determined at room temperature (25°C) using a pair of glass chambers (20 mL in volume of each chamber and 6.6 cm^2 in cross section), which contained water in one chamber and 1 mol/L MeOH solution in another chamber. The membrane was set between two chambers. The methanol permeability was obtained by periodically measuring the methanol concentration in the water chamber using a gas chromatograph (GC-8A, Shimadzu, Japan). The methanol permeability P (cm^2/s) through the membrane was given by¹⁵

$$P = DK = \frac{1}{A} \frac{C_B(t)}{C_A(t - t_0)} V_B L \quad (3)$$

where A (cm^2) and L (cm) are the membrane area and thickness, respectively, C_A (mmol/L) is the concentration of the methanol in the methanol chamber, V_B (mL) is the water volume in the water chamber, and t_0 is the time lag.¹⁵ D and K are the methanol diffusivity and partition coefficient between the membrane and the adjacent solution. DK was the permeability, which was evaluated from the slope of the linear line in the plot of the methanol concentration in the chamber B (C_B , mmol/L) and permeation time t (s).

Differential scanning calorimetry measurements of water in membranes

A Perkin-Elmer DSC-7 was used to evaluate the states of water in the membranes. The surface of the

water-swollen membrane piece was wiped with paper and then weighed before sealing the sample hermetically in an aluminum differential scanning calorimetry (DSC) pan. An empty pan with a lid was used as a reference. The samples were equilibrated at -50°C for 5 min and then heated at a ramp rate of $5^\circ\text{C}/\text{min}$ up to 10°C using the standard DSC mode.

RESULTS AND DISCUSSION

Particle size and IEC

The sizes of PS and PSSA microspheres were measured by DLS. The results show that the average size of PS and PSSA microspheres was 200 and 260 nm, respectively. Compared with PS microspheres, after sulfonation, the microspheres became a little larger. This is, probably, because of the increase of sulfonic groups on the surface of the microspheres and of their swelling by water uptake.

The FTIR absorbance spectra of PS and PSSA microspheres are shown in Figure 2. PSSA microspheres show a peak around 1040 cm^{-1} due to the symmetric stretching vibration of the SO_3 group and a relatively broad peak around 1182 cm^{-1} due to the asymmetric vibration of the SO_3 group.¹³ For both two samples, a broad peak was detected at $\sim 3400\text{ cm}^{-1}$. This has been ascribed to stretching modes of hydroxyl groups of $-\text{SO}_3\text{H}$ groups and water molecules retained by the samples.¹⁶ The relative height change of peak at 1412 cm^{-1} , which is ascribed to the *para*-disubstituted benzene,¹⁷ indicates that the *para* substitution reaction occurred. All these results demonstrate the successful sulfonation of PS microspheres.

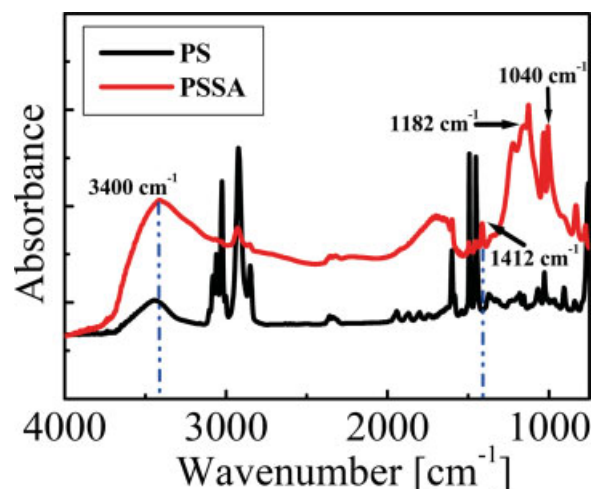


Figure 2 FTIR absorption spectra of PS and PSSA microspheres. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

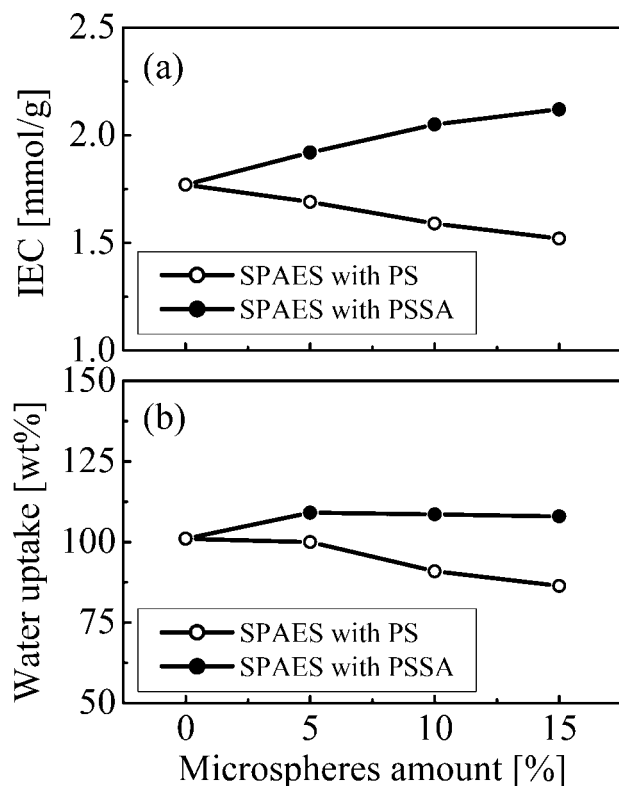


Figure 3 Effect of the microsphere amount on the ion-exchange capacity (IEC) (a) and water uptake of the composite membranes (b).

To determine the degree of the sulfonation, the IEC of PSSA microspheres was measured by titration. It was 5.3 mmol/g, whereas that of PS microspheres did not have any IEC.

Membrane IEC and water uptake

The composite membranes were prepared by casting the SPAES solution containing the PS or PSSA microspheres. Proton conductivity and methanol permeability across a membrane generally depend on the amount and behavior of water in the membrane to a large extent.¹⁸ The IEC and water uptake of the composite membrane are closely related to the membrane properties and play important roles in the membrane performance. Figure 3(a,b) shows the IEC and water uptake of the composite membranes as a function of the addition of the microspheres. An addition of PS microspheres in the membrane decreased the IEC and water uptake of the composite membrane. This is because PS microspheres are hydrophobic and cannot keep water. When the PS particle content in the membrane increased, the substantial content of SPAES polymer in the membrane consequently decreased. Thus, the IEC and water uptake of the membranes decreased. On the other hand, with the increase of PSSA microspheres in the

membrane, the IEC and water uptake of the membranes increased. This is due to the high IEC of the PSSA microspheres. When they were added in the membrane, the content of the SO_3H groups in the composite membrane increased, which led to the improvement of the IEC of the membrane. The SO_3H groups of the PSSA can hold water molecules, resulting in the high water uptake of the composite membranes.

The mechanical strength of the membranes in the wet state was measured with a tensile apparatus (AGS-J, Shimadzu Co., Japan). The results were shown in Table I. The tensile strength and elongation of both PS and PSSA composite membranes were reduced with the increase of the microspheres. However, when PS was added in the membrane, the Young's modulus of the membranes was improved. This may be attributed to the low water uptake of the PS composite membranes.

The thermal stability of the membranes was investigated with thermogravimetric analysis (TGA) at a heating rate of $10^\circ\text{C}/\text{min}$ under air flowing at 50 mL/min. The TGA data showed that the incorporation of PS and PSSA particles did not affect the thermostability of membrane so much.

Proton conductivity of membranes

The proton conductivity of the composite membranes as a function of RH is shown in Figure 4(a,b). The proton conductivity slightly decreased when the addition of the PS was 5 wt %. However, when the amount of PS was 15 wt %, the proton conductivity decreased sharply. Many reports described that there are two proposed mechanisms for proton transport through a PEM.¹⁹ One is the hopping or jumping (Grotthuss) mechanism, in which a proton passes along fixed sulfonic acid sites and a chain of water molecules. One proton adds to one side of a water molecule, causing another different proton jump off the other side to another water molecule. The other is the vehicle mechanism, in which a proton combines with solvent molecules, yielding a complex such as H_3O^+ , and then this complex is transported

TABLE I
Mechanical Properties of Composite Membranes

Polymer	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
SPAES bare	16.3	155.6	85.5
5%-PS	14.0	177.7	48.1
10%-PS	12.6	175.9	33.5
15%-PS	12.0	194.6	25.0
5%-PSSA	14.0	135.1	62.8
10%-PSSA	11.1	100.3	42.3
15%-PSSA	10.5	102.3	40.1

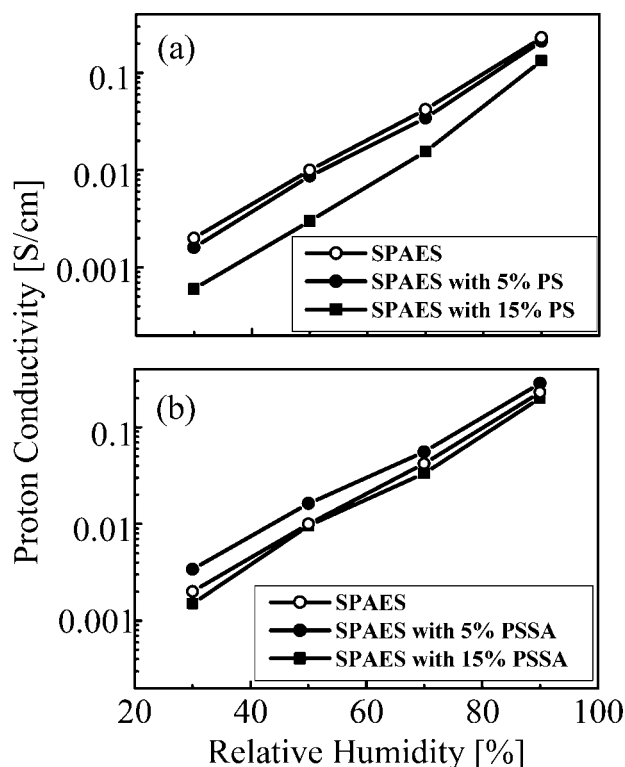


Figure 4 Relation between proton conductivity and relative humidity (a) addition of PS microspheres and (b) addition of PSSA microspheres.

through a membrane. In our PS composite membranes, the water uptake decreased. This implies that the water available for either as the hopping or as the vehicle might be reduced. As a result, the proton conductivity decreased. When the amount of PS was 15 wt %, inside the membrane, there were so many hydrophobic microspheres that prevented the transport of the protons through the membrane. Hence, the proton conductivity decreased sharply.

The proton conductivity of SPAES/PSSA composite membranes at varied RH is shown in Figure 4(b). When the addition of PSSA was 5 wt %, the proton conductivity was improved compared with the bare SPAES membrane. The improvement by the PSSA microspheres was more pronounced at the low RH. The increase in the conductivity would be attributed to the high water uptake and the high IEC induced by the PSSA microspheres. According to the proton-conducting mechanism, water acts as the vehicle or the hydrogen-bonding network. Therefore, the proton conductivity increased with the increase of the water uptake. In addition, because the excess protons originate from the immobile acidic functional groups,²⁰ the sulfonation of PS provided immobile acidic groups to the membrane. The sulfonate groups not only increased the IEC but also promoted the proton transports across the membrane. Although the IEC and water uptake of the composite

membrane was also high at a PSSA addition of 15 wt % (Fig. 3), the proton conductivity decreased adversely. It might be because when the PSSA content was too high, the path length for proton transport increased greatly, as the proton cannot be transported inside the PSSA microspheres, and the proton conductivity became low.

The effect of the addition of the two microspheres on the proton conductivity at the 50% RH condition was shown in Figure 5. The proton conductivity decreased slightly at first and then decreased sharply with the increase of PS microspheres in a membrane. On the other hand, with the increase of PSSA microspheres in a membrane, the proton conductivity increased first and then decreased. At low humidity, all the membranes were likely to be dehydrated. However, the water molecules, which were chemically bonded with sulfonic acid groups in a membrane, were relatively difficult to be evaporated. In another words, membranes with high IEC would keep more water than membranes with low IEC at low humidity. For SPAES/PSSA composite membranes, as the amount of sulfonic acid groups increased, the composite membranes would keep more water than a bare membrane. Therefore, the proton conductivity first increased. For further addition of PSSA, the pass of the protons through the membranes became difficult, and the proton conductivity decreased.

Methanol permeability of membranes and proton/methanol selectivity in the permeation

Methanol permeability of the composite membranes is presented in Figure 6. As the loading of the PS microspheres increased, the methanol permeability decreased. One of the possible reasons is that the addition of the hydrophobic PS microspheres

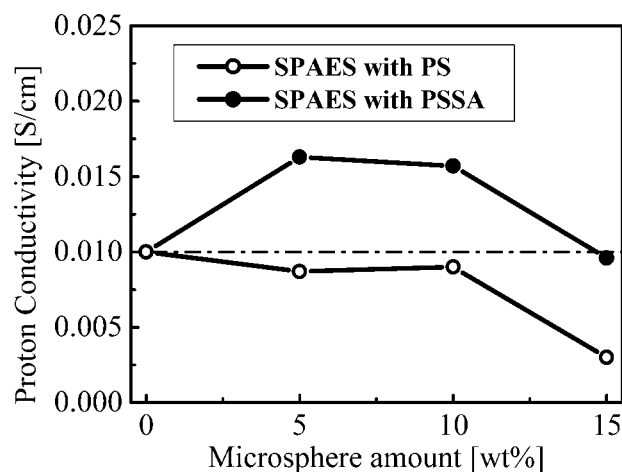


Figure 5 Proton conductivity of membranes with addition of microspheres at 50% RH.

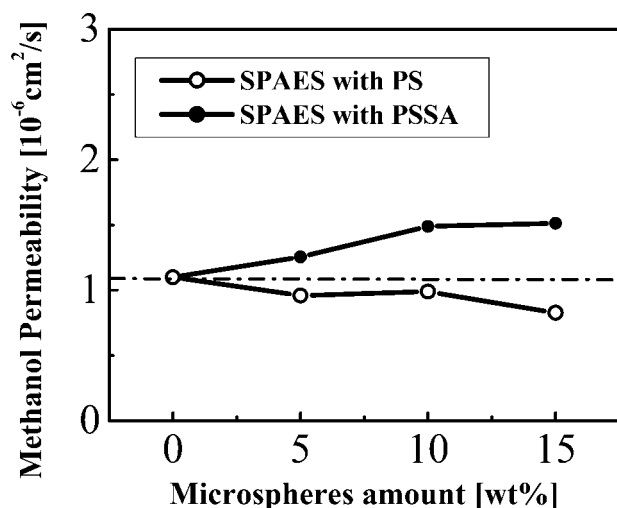


Figure 6 Methanol permeability of membranes with addition of PS and PSSA microspheres.

increased the tortuosity of the permeation path of methanol in the membrane. In addition, the addition of the PS microspheres decreased the water uptake of the membrane. We also observed that the increment in the PSSA content led to an increase in the methanol permeability of the composite membrane. Several reports suggested that methanol permeates through a water-rich or a hydrophilic domain in a membrane and that the hydrophobic domain hinders the methanol transport.^{15,17} The modification of the SPAES membrane with PSSA microspheres improved the water uptake of the membrane, resulted in enlarging the hydrophilic domain in the membrane. The enlarged hydrophilic domain might overcome the expelling force of a hydrophobic domain toward methanol, which then resulted in the increased methanol permeability.

Proton/methanol selectivity is defined as the ratio of the proton conductivity to methanol permeability. This is often applied to evaluate the potential performance of a PEM in DMFCs.^{21,22} An ideal PEM for a DMFC is expected to have high proton conductivity and low methanol permeability. Figure 7 shows the methanol permeability as a function of the proton conductivity at 50% RH. For comparison, the data of a commercial Nafion[®] 117 membrane was also plotted in the figures. The slope of the drawn lines indicated the selectivity of a bare SPAES membrane and the commercial Nafion 117 membrane. Except for the composite membrane with 15 wt % PS, all the other composite membranes showed higher selectivity than the commercial Nafion 117 membrane. The SPAES membrane with 5 wt % PSSA microspheres has the highest selectivity among all the membranes tested. When more PSSA microspheres were added to membranes, the proton conductivity was not improved greatly, and the metha-

nol permeability increased sharply. As a result, the selectivity decreased. When the addition of PS microspheres was 5 and 10 wt %, the selectivity of the membrane was almost the same as the bare SPAES membrane, because the methanol permeability reduced and the proton conductivity remained almost the same as that of a bare SPAES membrane. With 15 wt % addition of PS microspheres, the selectivity was lower than a bare SPAES membrane.

Further experiment is necessary to test these composite membranes in the practical application of DMFC.

DSC measurements of water in membranes

There are three different states of water in a proton exchange membrane.^{15,17,23} The first is non-freezing-bound water, which strongly binds to a polymer chain and plays the role of a plasticizer. The second type is freezing-bound water, which weakly binds to a polymer chain and interacts weakly with non-freezing-bound water. The third type is free water, which does not bind to a polymer and behaves as bulk water. The states of water in a membrane affect the membrane performance greatly. It has been reported that a low fraction of free water in membranes generally leads to a low electro-osmotic drag under fuel cell operation, resulting in low methanol permeabilities.²⁴ Therefore, the study of states of water might be attractive. It has been shown that the bound water cannot be detected by DSC and that the melting endotherm observed in a DSC thermogram near 0°C is due to the free and freezing-bound water.^{15,23} In the DSC measurements, two neighboring melting peaks were observed. On heating, the first broad peak was observed at the temperature lower than 0°C, which belongs to the freezing-bound water. The second sharp peak, which was observed

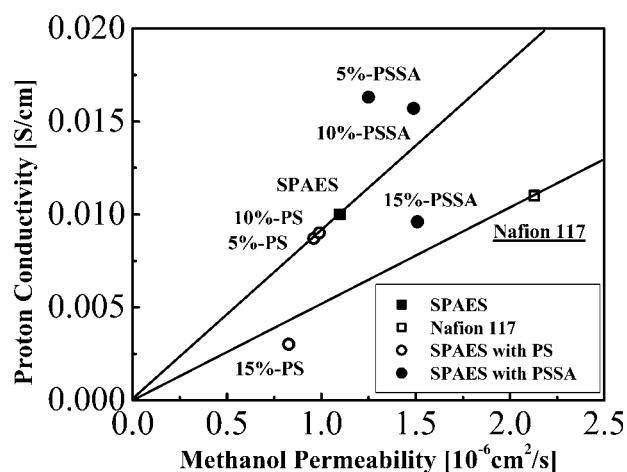


Figure 7 Proton/methanol selectivity of membranes with addition of PS and PSSA microspheres at 50% RH.

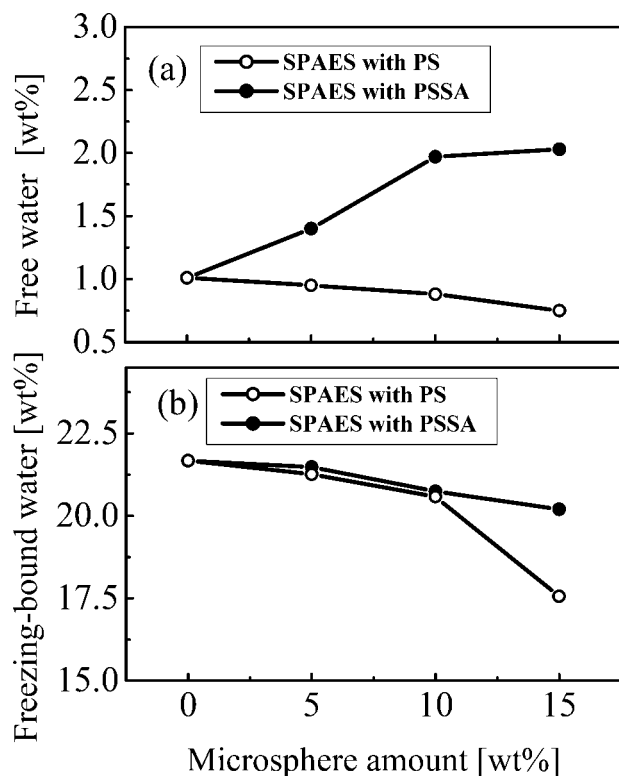


Figure 8 Effect of the microsphere amount on free water content (a) and freezing-bound water contents in the membranes (b).

near 0°C, was derived from the free water. The contents of two water states can be calculated from the ratio of the endothermic peak areas to the heat of fusion (334 J/g) for pure water. Figure 8(a,b) shows the water contents (wet basis) corresponding to the free and freezing-bound water. When the SPAES membrane was modified with PS microspheres, the free water content of the membranes decreased. This can be explained by the hydrophobic space produced by the PS microspheres. Because the free water in a membrane acts as a vehicle for proton and methanol transport,¹⁵ the addition of the PS microspheres decreased the free water content and resulted in the decrease of methanol permeability in this study. On the other hand, when adding the PSSA microspheres in the SPAES membrane, both the total water content and the free water content of the membranes increased simultaneously, which resulted in the increase of proton conductivity as well as methanol permeability. It can also be observed that the increment in both PS and PSSA contents led to the decrease of the freezing-bound water content of the composite membranes. The freezing-bound water existed around the bound water and the clusters of the polymer network.²⁵ For the composite membranes, the actual content of the SPAES polymer became low due to the increase of microspheres in membranes and the relative clusters

content decreased. Thus, the freezing-bound water content decreased.

CONCLUSIONS

Two kinds of organic microspheres, PS and PSSA, were introduced to SPAES membranes for a PEM. PSSA microspheres with 5.3 mmol/g IEC were synthesized by direct sulfonation of the PS microspheres.

Compared with a bare SPAES membrane, SPAES/PS composite membranes showed lower proton conductivity and methanol permeability due to the hydrophobicity of the PS microspheres. On the contrary, SPAES/PSSA composite membranes showed higher proton conductivity because of the improvement of the IEC by adding PSSA microspheres. This study indicates the important role of the particle surface as an additive in the PEM performance.

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